Electrolytic Determinations and Separations with the use of a Rotating Anode

THESIS

PRESENTED TO THE FACULTY OF THE DEPARTMENT OF PHILOSOPHY OF THE UNIVERSITY OF PENNSYLVANIA IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

BY

JULIA LANGNESS, B.S.

CARLETON COLLEGE, MINN.

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INTRODUCTION

In this thesis are presented numerous new data obtained by the use of a rotating *dish* anode in the electrolysis of several metallic salt solutions. Curves accompany the various experiments to show more clearly the progressive deposition of metal. Such data cannot fail to be of great service to the analyst.

The remarkably short periods in which copper, silver, nickel, and zinc are precipitated by the use of the *dish* anode leaves no doubt as to the superiority and advantage of electrolytic methods over ordinary gravimetric procedures.

The separations of metals using the rotating anode make the rapid methods even more useful. There seems little doubt but that in a short time many of the electrolytic separations now quite satisfactory with stationary electrodes will be further improved by the addition of conditions under which they can be executed with rotating anodes, using increased current and pressure, thus decreasing the time factor to a minimum.

EXPERIMENTAL PART

I. A New Form of the Rotating Anode used in Electro Analysis.

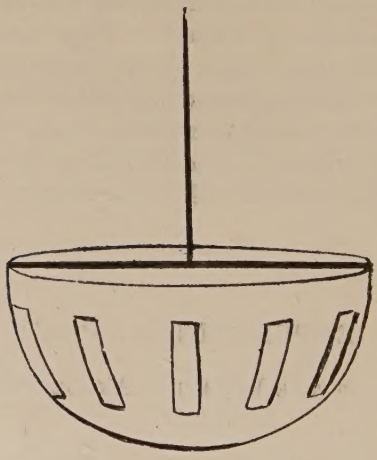
(a) *Description of Anode.*

The spiral anode used and described by Exner has been employed in nearly all the work done in this laboratory on the rapid precipitation of metals in the electrolytic way.

It was with the view of still further reducing the time element that a new form of anode was devised, following a brief description of which, will be recorded a series of experiments illustrating its advantage over older forms.

For the sake of comparison it may be well to recall the apparatus ordinarily used. The anode consists of a stout platinum wire bent at one end into a flat spiral of several revolutions and having a diameter of about two inches. The spiral during the electrolysis is made to rotate, and dips below the surface of the electrolyte contained in a platinum dish, which is made the cathode.

The dish employed as cathode is illustrated in the third edition of Smith's "Electrochemical Analysis" page 77. It has a diameter of about 9.5 cm, a depth of 4.8 cm; and a capacity of about 200 cc.; but in ordinary determinations the liquid used is only about 125 cc., and the surface on which the metal is deposited approximates 100 sq. cm.



Dish Anode.

The new anode is a platinum dish of the same general form as the cathode (see Figure 1). It is about 7 cm. in diameter and 3 cm. deep. Its sides are provided with ten slits perpendicular to the edge, each slit about 1.8 cm. long, and .5 cm.

wide. These openings, together with a circular opening 1.3 cm. in diameter in the bottom of the dish, insure free circulation of the liquid.

The anode is held in position by a stout platinum rod, and it is so adjusted that it is equidistant from the sides of the cathode.

During the rotation of the anode the liquid is all contained within the space bounded by the cathode and the outer surface of the anode, no liquid remaining within the inner dish. It is therefore evident that the dilution in this case must be much less than when the spiral anode is employed. The volume of the electrolyte should not exceed 65 cubic centimeters.

When properly adjusted there is no splashing of the liquid and consequent loss of the electrolyte, as one might at first suppose there would be, nor is there any danger of incomplete precipitation due to liquid adhering to the inside of the anode, the decanted liquid showing no trace of the metal when subjected to tests.

(b) *Determination of Metals.*

COPPER.

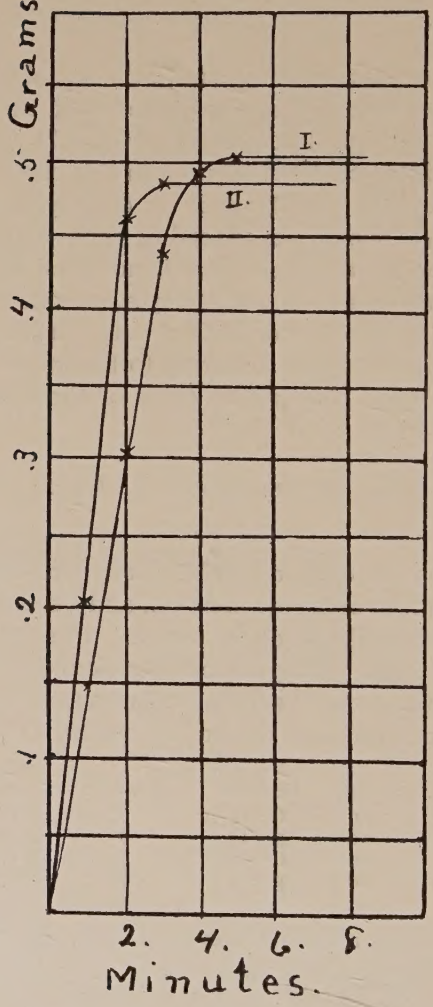
A solution of copper sulphate was prepared containing about 0 .5035 gram of copper in 25 cc., and a series of determinations were made with the *spiral* anode. The most satisfactory conditions for rapid precipitation were found to be as follows: To 25 cc. of the copper sulphate solution add 1 cc sulphuric acid (dil. 1:10), and 100 cc. boiling water, and electrolyze.

No.	Volts.	Amperes.	Time, min.	Wt. of Cu in grams.
1	10	6—13	7	0.5038
2	10	5—13	7	0.5037
3	10	6—13	7	0.5034
4	10	5—13	7	0.5035

The perfectly adherent deposits were dark red in color, with a beautiful velvety appearance.

Observing the above conditions the following time curve, (*Curve No. I*) was determined:

Copper —
Curves I and II.



Volts.	Amperes.	Time, min.	Wt. of Cu in grams.
10	5.6	1	0.1493
10	5.6	2	0.3019
10	5.6	3	0.4371
10	5.6	4	0.4925
10	5.6	5	0.5029

Using the *dish* anode, with the same electrolyte, and diluting to about 60 cc., these results were obtained:

No.	Cu present in grams.	Volts.	Amperes.	Time, min.	Wt. of Cu in grams.
1	0.4884	7+	10—15	4	0.4883
2	0.4884	8	10—16	3	0.4884
3	0.4884	8	10—16	5	0.4887
4	0.4884	8	10—	2	0.4634
5	0.4884	8	10	1	0.2010

The character of the deposit was the same as when the spiral was used. *Curve II* is constructed from above results.

When the *spiral* anode was used and nitric acid added as electrolyte the best results obtained were those in which ½ cc. of the acid was added to 25 cc. of the copper sulphate solution, and the solution diluted to 125 cc. with boiling water, (25 cc. of the solution contained about 0.4876 gram of copper). Brilliant, crystalline, adherent, deposits were obtained.

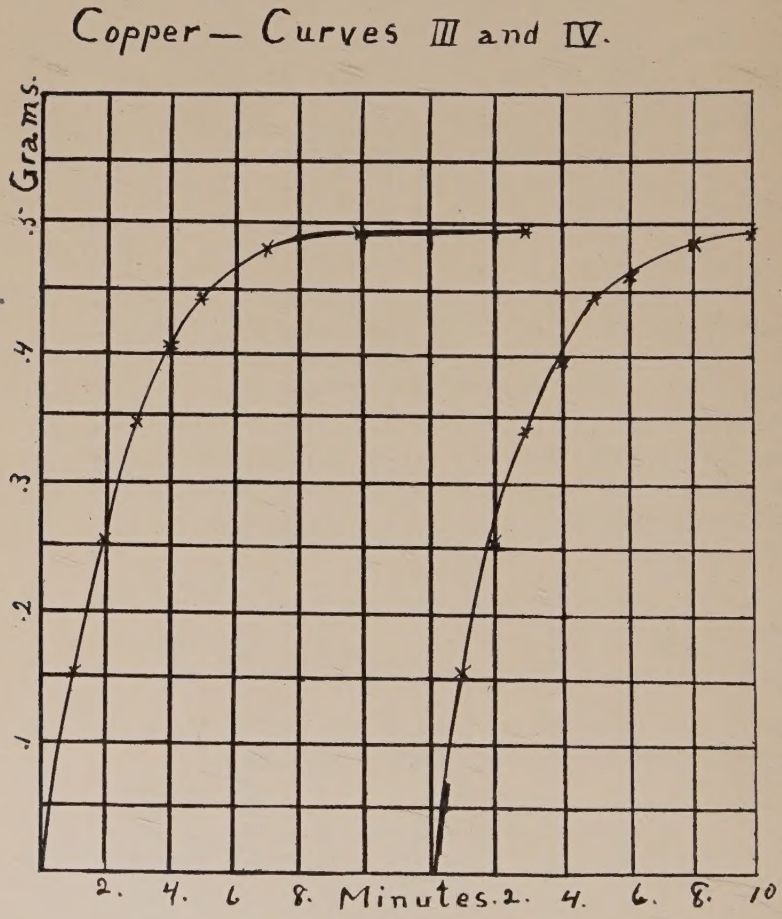
No.	Volts.	Amperes.	Time, min.	Wt of Cu in grams.
1	8	7	15	0.4878
2	8	7	15	0.4877
3	8	8	15	0.4875
4	8	8	10	0.4875

The following time curve determinations show that ten minutes are required for complete precipitation.

No.	Volts.	Amperes.	Time, min.	Wt. of Cu in grams.
1	8	7—8	1	0.1507
2	8	7—10	2	0.2518
3	8	7—11	3	0.3418
4	8	7—11	4	0.3960
5	8	7—11.5	5	0.4486
6	8	7—12	6	0.4654
7	8	7—12	8	0.4852
8	8	7—12	10	0.4875

See *Curve III* for graphic representation.

Using the *dish* anode with the same electrolyte the deposition of 0.4817 gram of copper was complete in six minutes, with a pressure of 8 volts and 16 amperes.



When 25 cc. copper sulphate solution containing 0.4967 gram of copper, to which was added 1.2 gram of ammonium nitrate and 25 cc. ammonia were diluted to 125 cc., heated to boiling,

and electrolyzed, complete precipitation, using the *spiral* anode, required about fifteen minutes, as per table below and *Curve* IV.

No.	Volts.	Amperes.	Time, min.	Wt. of Cu. in grams.
1	8	9	1	0.1508
2	8	9	2	0.2520
3	8	9	3	0.3455
4	8	9	4	0.4023
5	8	9	5	0.4422
6	8	9	7	0.4802
7	8	9	10	0.4914
8	8	9	15	0.4963

The deposits were bright and adherent.

With the same electrolyte 0.4824 g. copper in solution was deposited in six minutes with 6 volts and a current of 17 amperes, using the *new* anode.

The *dish* anode was also employed in depositing copper from a cyanide solution. A slight excess of potassium cyanide was added above that required to precipitate the copper and redissolve the precipitate. To that solution were added 10 cc. ammonia, and in six minutes, using 7 volts and 15 amperes, 0.4883 gram of copper was deposited in a beautiful burnished form. No time curve was prepared.

SILVER.

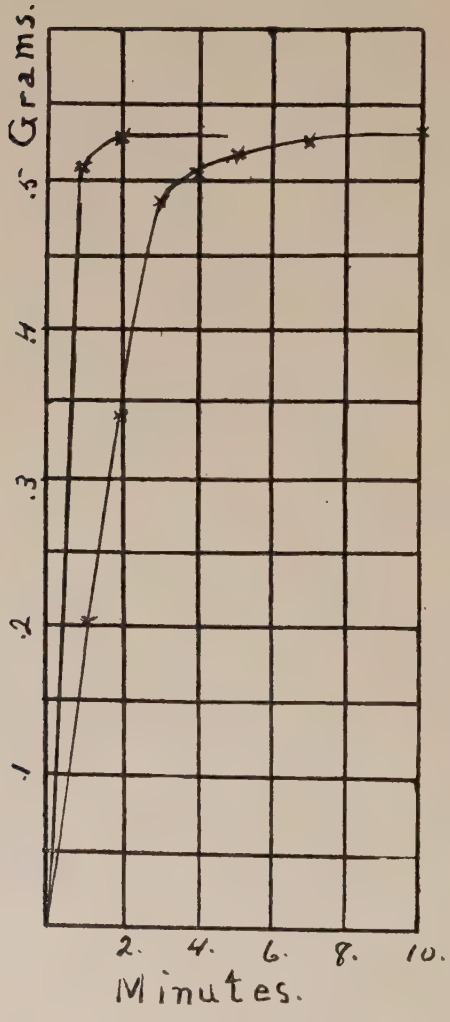
Silver was then tried and with the most satisfactory results. The silver from a silver nitrate solution was precipitated and redissolved in potassium cyanide, and an excess of two grams potassium cyanide added in each determination, the solution diluted as usual, heated almost to boiling, and electrolyzed.

The following table and corresponding curve (*No. V*) show results obtained by the use of the *spiral* anode.

No.	Volts.	Amperes.	Time, min.	Wt. of Ag. in grams.
1	5	2.8	1	0.2046
2	5	2.8	2	0.3391
3	5	2.8	3	0.4858
4	5	2.8	4	0.5043
5	5	2.8	5	0.5225
6	5	2.8	7	0.5270
7	5	2.8	10	0.5301

Silver—

Curves V and VI.



The precipitation was complete in ten minutes.

The deposits were chalk-white, and spongy in the bottom of the dish, but adherent. With the *new* anode, using same solution, and adding 3 grams of potassium cyanide, the .53 gram of silver was deposited in two minutes, all but a very small quantity of which was precipitated during the first minute. See *Curve VI* constructed from results given in table below.

No.	Volts.	Amperes.	Time, min.	Wt. of Ag. in grams.
1	5	10	4	0.5304
2	5	6	4	0.5306
3	5	8	3	0.5306
4	5	9	2	0.5304
5	5	9	1	0.5116

The great differences in current strength in the above series are due mainly to the variation in distance between the electrodes, a small decrease in distance causing a large rise of the current, the pressure being kept constant.

NICKEL.

A few determinations of nickel from a solution containing ammonium sulphate show that half a gram of that metal may be precipitated in five minutes using the *dish* anode.

To 25 cc. of the nickel solution containing 0.5004 gram of of the metal were added 3 grams of ammonium sulphate dissolved in water and 20 cc. ammonia, the solution then diluted to 60 cc. and heated almost to boiling.

No.	Volts.	Amperes.	Time, min.	Wt. of Ni. in grams.
1	6.	11—16	6	0.5005
2	6.5	11—14	5	0.5002

ZINC.

This metal was also tried, and it was found that a quarter of a gram of the metal could be deposited in three minutes, using *dish* anode and conditions indictated for experiment No. 2 in the series below.

No.	NaOH added.	Volts.	Amperes.	Time, min.	Wt. of Zn in grams.
1	5 g.	5	10	6	0.2472
2	4 g.	6	13	3	0.2476
3	8 g.	5	13	8	0.2472

II. The Precipitation of Platinum, Palladium, and Rhodium by use of a Rotating Anode.

(a) *Platinum.*

Platinum has long been known to be completely precipitated by means of the electric current, and, while the ordinary electrolytic methods for the determination of this metal are very satisfactory, they require considerable time,—four to five hours for the precipitation of .1 to .2 gram. By agitating the electrolyte the complete deposition of the same amount may be accomplished in a few minutes, as shown by the following experiments, in which a solution of potassium platinum chloride was used, 25 cc. of the solution containing about 0.0953 gram of platinum. The metal was deposited on a silver coated dish. The *dish* anode, described on page 4, was employed and was made to rotate during the electrolysis.

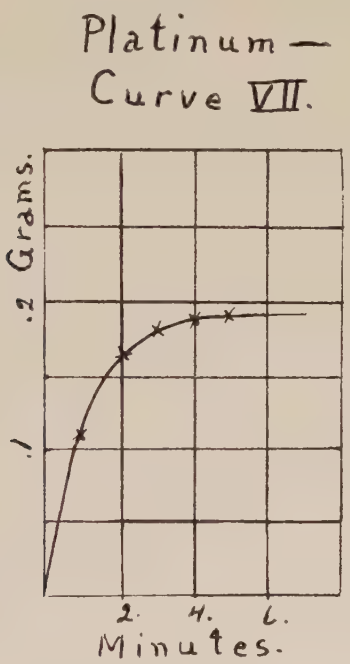
No.	H_2SO_4 (dil. 1: 10) in cc.	Volts.	Amperes.	Time, min.	Wt. of Pt. in grams.
1	5	7	14	4	0.0956
2	5	8	14	3	0.0907
3	5	7	14	1	0.0821
4	5	5	10	7	0.0953
5	5	6	17	3	0.0932
6	2.5	10	16	3	0.0952
7	2.5	10	17	2	0.0926

In numbers 1, 4, and 6 the precipitation was complete. The deposits were dark gray in color and perfectly adherent. The great difference in voltage and amperage in the above experiments is due mainly to variations in electrode distance.

Reproducing the conditions of 6 and 7, doubling the amount of the solution, and diluting to 60 cc., the following experiments gave the results from which *Curve No. VII* was constructed.

No.	H_2SO_4 (dil. 1: 10) in cc.	Volts.	Amperes.	Time, min.	Wt. of Pt. in grams.
1	2.5	10	16	3	0.1855
2	2.5	10	18	4	0.1973
3	2.5	10	17	5	0.1904
4	2.5	10	18	2	0.1734
5	2.5	10	17	1	0.1158

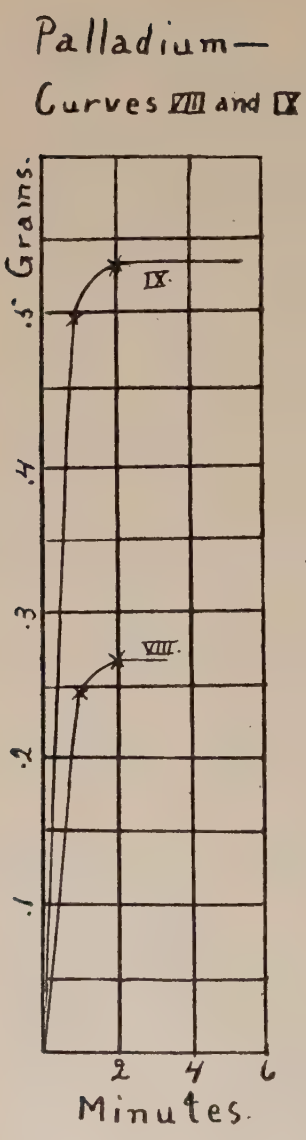
The platinum was completely precipitated in five minutes.



(b) *Palladium.*

This metal was precipitated from a solution of palladammonium chloride, Pd. $(NH_3\ Cl)_2$. A quantity of this salt was dissolved in ammonia and diluted so that 10 cc. of the solution contained about 0.268 gram of palladium.

The deposits were usually made on silver coated dishes, and the rotating *dish* anode was employed.



To 10 cc. of the palladium solution were added 20 cc. boiling ammonia, and the whole diluted to 60 cc. with boiling water and electrolyzed.

No.	Volts.	Amperes.	Time, min.	Wt. of Pd. in grams.
1	5—6	2+	18	0.2682
2	11	5	10	0.2680
3	17	7	5	0.2682
4	17	10	3	0.2678
5	17	10	2	0.2678
6	17	9	1	0.2476
7	17	10	2	0.2683
8	17	10	2	0.2680
9	17	10	2	0.2681

The precipitation was complete in all except the sixth experiment. The deposits were gray and spongy, but perfectly adherent. In the last three the metal was deposited directly on the platinum dish, and was removed by a warm mixture of chromic acid and potassium chloride.

Another series of determinations was made by doubling the amount of the palladium solution.

No.	NH_4OH in cc.	Dilution.	Volts.	Amperes.	Time, min.	Wt. of Pd. in grams.
1	20	60 cc.	15	14	3	0.5358
2	20	60 cc.	17	14—20	2	0.5357
3	20	60 cc.	17	14—20	1	0.4966

The above recorded determinations of palladium speak for the accuracy of the method. With no other metal does the rapid electrolytic determination give more satisfactory results. The

character of the deposit is excellent, the time element almost annihilated, and the range of conditions within which the complete precipitation is possible, is large; a high current, however, being necessary for the speediest deposition. *Curves VIII and IX* were constructed from data given above. Another series of experiments in which no ammonia was added gave very satisfactory results both as to time and character of deposits.

(c) *Rhodium.*

The rapid precipitation of rhodium was found to be best accomplished from a solution of sodium rhodium chloride Na_2RhCl_6 to which a few drops of sulphuric acid had been added.

In the first four determinations of the following series 10 cc. of the rhodium solution (about 0.0576 gram of rhodium), acidified with 2.5 cc. sulphuric acid (dil 1:10), was diluted to 105 cc. with boiling water, and electrolyzed, using a *spiral* anode; while in the last three, using the dish anode, the solution was diluted to about 60 cc. The metal was deposited on a silver coated dish.

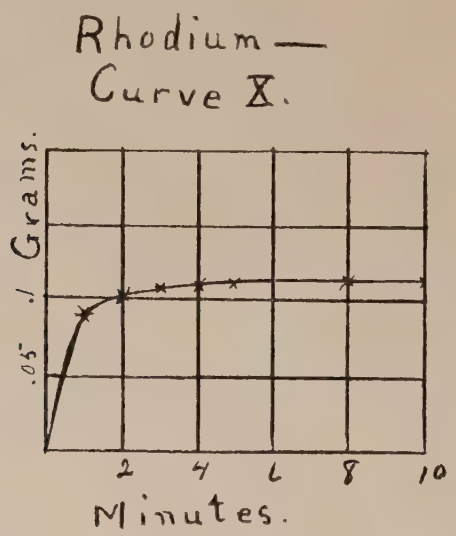
No.	Volts.	Amperes.	Time, min.	Wt. of Rh. in grams.
1	7.	8	15	0.0577
2	7.5	8	10	0.0580
3	8.	9	10	0.0575
4	8.	9	7	0.0576
5	8.	15	4	0.0573
6	6.	11	4	0.0563
7	7.	14	4	0.0567

In all but the sixth and seventh the precipitation was complete. The deposits were adherent and almost black in color.

Doubling the quantity of the rhodium solution the following time curve determinations were made using the *dish* anode.

No.	Volts.	Amperes.	Time, min.	Wt. of Rh. in grams.
1	7	15	1	0.0896
2	7	15	2	0.1006
3	7	15	3	0.1104
4	7	15	4	0.1128
5	7	15	5	0.1141
6	7	15	8	0.1152
7	7	15	10	0.1153

See *Curve X* for plotted results.



III. Separations.

(a) *Gold from Platinum.*

1. Sodium Sulphide as Electrolyte.

Platinum was precipitated and redissolved in sodium sulphide and the hot solution electrolyzed with a pressure of 5 volts, giving 7 amperes current. No deposit was obtained in 15 minutes. This suggested a possible separation from gold which, as is known, may be precipitated from a similar solution.

A mixture of the two sulphides in solution, containing about 0.05 gram of gold and 0.09 gram of platinum, was accordingly subjected to electrolysis. After 15 minutes, when the current was interrupted no deposit whatever could be seen. The experiment was repeated with the same result. On reweighing the dishes, which showed no indication of a deposit, it was found that they had increased in weight by 0.0340 gram and 0.0400 gram. The beautiful alloy of gold and platinum was given no further attention as the object in view was the finding of a method of separation of the two metals.

2. Potassium Cyanide as Electrolyte.

As the cyanide electrolyte affords a means of separating gold from platinum in the slow way, it was thought probable that a rapid separation might be possible from the same electrolyte. In the following determinations 5 cc. gold chloride solution containing about 0.0462 gram of gold, and 25 cc. platinum solution containing about .094 gram of platinum were employed. A *spiral* anode was used in these separations. The solution was diluted to about 125 cc. and heated almost to boiling in each case.

No.	Au sol. in cc.	Pt. sol. in cc.	KCN, in grams.	Volts.	Amperes.	Time, min.	Wt. of Au.
1	5	10	1.5	6	2	15	0.0464
2	5	10	1.5	6	2	20	0.0462
3	5	10	2.	6+	2.5	12	0.0464
4	10	25	2.	6	2.5	20	0.0931
5	10	25	2.	6	2.5	15	0.0930
6	10	25	2.	6	2.5	10	0.0932
7	20	25	2.	6	2 5	15	0.1863

(b) *Gold from Palladium.*

Gold was separated from palladium from a cyanide solution containing about equal amounts of the two metals. The solution was diluted to about 125 cc. with boiling water and electrolyzed. The following three determinations show satisfactory conditions for the separation.

No.	Au sol. in cc.	KCN, in grams.	Volts.	Amperes	Time, min.	Wt. of Au.
1	5	1	6	2	10	0.0464
2	5	1	6	2	30	0.0462
3	10	1.5	6	2	30	0.0932

(c) *Copper from Platinum.*

A series of determinations showed that copper can be precipitated free from platinum in a solution containing the two metals, when 3 grams potassium cyanide and 10 to 20 cc. ammonia are added. When the ammonia was omitted a faint trace of platinum was deposited with the copper.

No.	Cu sol. in cc.	Cu present in grams.	KCN in grams.	NH_4OH in cc.	Volts.	Amperes.	Time, min.	Wt. of Cu.
1	10	.1290	3	10	5	3.5	35	0.1290
2	10	.1290	3	10	5	3	30	0.1295
3	10	.1290	3	20	5	3	30	0.1291
4	10	.1290	3	20	5	3	60	0.1294

In the fourth determination, in which the current was passed through the solution for a whole hour, a very slight trace of platinum was detected in the deposit.

(d) *Copper from Palladium.*

A long series of determinations were made with widely varying conditions, but no complete separation was obtained.

(e) *Silver from Platinum.*

This separation is best accomplished from a solution containing 1.5 gram potassium cyanide. The silver present in solution in the following determinations was 0.1183 gram.

No.	Volts.	Amperes.	Time, min.	Wt. of Ag.
1	3	.25—.05	20	0.1181
2	3	.25—.05	20	0.1180
3	3	.25—.05	25	0.1180
4	3	.25—.05	20	0.1182
5	3	.25—.05	20	0.1183

(f) *Silver from Palladium.*

An attempt to separate these two metals from a cyanide solution met with no success.

(g) *Silver from Copper.*

It was found that silver and copper may be separated with ease from a cyanide solution by means of the rotating anode. 2 grams potassium cyanide should be added.

No.	Volts.	Amperes.	Time, min.	Wt. of Ag.
1	2.5	.35—.1	15	0.1184
2	2.5	.4—.1	20	0.1184
3	2.2	4—.1	20	0.1183

(h) *Silver and Copper from Platinum.*

From a mixture of the three metals in a solution containing 2 grams potassium cyanide, the silver may first be removed and then the copper. In each of the following experiments the solution contained about 0.1314 gram copper and 0.1183 gram silver.

No.	Volts.	Amperes.	Time, min.	Weight of metal found.
1	2.5	.40—.08	15	0.1183 g. silver.
	5.	3.	35	0.1311 g. copper.
2	2.5	.45—.08	15	0.1182 g. silver
	5.	3.	35	0.1320 g. copper.

The silver deposits were free from copper and the copper deposits showed no trace of silver or platinum.

(i) *Silver from Nickel.*

Two separations were made from solutions containing 1.5 gram potassium cyanide.

No.	Volts.	Amperes.	Time, min.	Wt. of Ag.
1	2.5	.4—.07	20	0.1184
2	2.5	.4—.07	20	0.1185

(k) *Silver from Zinc.*

A solution of the two metals containing 2.5 grams potassium cyanide was used. Only two determinations were made, giving the results in the following table:

No.	Volts.	Amperes.	Time, min.	Wt. of Ag.
1	3	.35—08	20	0.1187
2	3	.3	20	0.1185

(l) *Silver from Copper in Coin.*

The ease with which silver may be separated from copper by means of the rotating anode suggested the rapid analysis of a silver coin by the same method.

A dime was cleaned and cut into four parts. One part was then weighed (0.7070 gram), dissolved in the least possible amount of nitric acid, the excess of acid evaporated, and the residue dissolved in water and diluted to 100 cc. To 25 cc. of this solution was added ½ gram potassium cyanide. The silver was first removed with a low current, and the decanted liquid after evaporation electrolyzed for the copper. The conditions used and results obtained are tabulated below.

No.	Volts.	Amperes.	Time, min	Wt. of metal.	Percent of metal.
1	3—2.5	.4—.06	35	0.1589 g. Ag	89.90 % silver.
	10	5.	10	0.0177 g. Cu	10.01 % copper.
2	3—2.5	.4—.06	45	0.1588 g. Ag	89.84 % silver
	10	6.	10	0.0180 g. Cu	10.18 % copper.

The complete analysis, including the weighing of the coin and the final weighing of the deposits, required about two and a half hours.

If two portions are taken, depositing the metals together in the one, and the silver alone in the other, the complete analysis can be made in an hour and a half, providing two dishes are available. One determination was made in that way. The coin weighing 0.5638 gram was dissolved in a small amount of nitric acid (less than 1 cc.). Part of the excess of acid was evaporated and a few drops of ammonia added to neutralize the

remaining excess. Two grams of potassium cyanide were then added and the solution diluted to 100 cc. 25 cc. of this solution diluted to about 125 cc. were electrolyzed for the silver and copper combined, and a second portion for the silver alone.

Volts.	Amperes.	Time, min.		
7	2	18	0.1409 combined weight of Cu and Ag	99.94 %
2.5	.5—.07	25	0.1268 weight of silver	90.00 %

ACKNOWLEDGMENT.

This investigation was conducted under the direction of Dr. Edgar F. Smith, and I wish to express to him my hearty thanks for his many valuable suggestions, his helpful encouragement and cordial interest throughout the work.